

A New Approximation Scheme in Quantum Mechanics

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Abstract

An approximation method which combines the perturbation theory with the variational calculation is constructed for quantum mechanical problems. Using the anharmonic oscillator and the He atom as examples, we show that the present method provides an efficient scheme in estimating both the ground and the excited states. We also discuss the limitations of the present method.

03.65, 31.15.P, 31.15.M

Typeset using REVTeX

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I. INTRODUCTION

In undergraduate quantum mechanics, students are taught generally two types of approximation schemes, the perturbation theory and the variational calculation. Each method is known to have its own advantages and limitations. The perturbation theory is applicable only when the perturbing potential is small, whereas the variational method lacks systematic means for improvement after the first approximation. Also, it is rather cumbersome and difficult to estimate the excited states in the variational method [1–4].

In this paper, we present an approximate scheme which combines the two approximation methods. It will be shown that the combined method carries the advantages of both methods and, at the same time, overcomes the deficiencies mentioned above. Actually, the concept of combining the two approximation methods is not entirely new. For instances, this concept has been used in lattice dynamics to obtain a better description of phonons in crystals [5]. In this approach, perturbation calculations were made on the basis of the variational self-consistent harmonic approximations. Also, in relativistic field theories, this approach was called the perturbation with variational basis and used to calculate effective Gaussian potentials and high order terms [6,7]. However, to the authors' knowledge, this concept has never been discussed in a plain quantum mechanical language understandable to undergraduate or graduate students who do not have knowledge of either lattice dynamics or relativistic quantum field theory. Therefore, we believe that developing this combined approximation scheme for quantum mechanical problems is not only pedagogically important, but also useful for real applications in quantum mechanical problems.

II. PERTURBATION WITH A VARIATIONAL BASIS

In a variational calculation, we first choose a trial function $\Psi(\lambda)$ as a function of a variational parameter λ for a given Hamiltonian H . Then, the ground state energy is estimated by minimizing the expectation value, $\langle \Psi_\lambda | H | \Psi_\lambda \rangle$ against λ . In the present formalism, we also

first choose a trial function $\Psi_n(\lambda)$. However, here, the choice of $\Psi_n(\lambda)$ is limited to the cases where a parent Hamiltonian H_λ , which carries $\Psi_n(\lambda)$ as exact eigenfunctions, can be found. We will discuss implications of this limitation of the theory below. We just assume here that such a parent Hamiltonian can be found for a given problem. Then we rewrite the original Hamiltonian, H as follows,

$$\begin{aligned} H &= H_\lambda + H - H_\lambda \\ &= H_\lambda + H' \quad , \end{aligned} \tag{1}$$

where $H' = H - H_\lambda$ is the perturbing Hamiltonian. Clearly, success of a perturbative calculation depends on how small H' can be made. In order to obtain an optimum H_λ , we first determine λ through the condition

$$\delta \langle \Psi_n(\lambda) | H | \Psi_n(\lambda) \rangle = 0. \tag{2}$$

Here, we note that this condition is not limited to the ground state, but is valid to all excited states also. Therefore, generally λ will be dependent on the state number n . Thus we express λ and H_λ as λ_n and H_{λ_n} respectively. Using the above notations, we carry out the standard perturbation calculation of E_n .

$$\begin{aligned} E_n &= \langle \Psi_n(\lambda_n) | H_{\lambda_n} | \Psi_n(\lambda_n) \rangle \\ &+ \langle \Psi_n(\lambda_n) | H' | \Psi_n(\lambda_n) \rangle \\ &+ \sum_{k \neq n} \frac{|\langle \Psi_k(\lambda_n) | H' | \Psi_n(\lambda_n) \rangle|^2}{E_n^{(0)}(\lambda_n) - E_k^{(0)}(\lambda_n)} \\ &+ \cdots \quad . \end{aligned} \tag{3}$$

Here $E_n^{(0)}(\lambda_n)$ is the n th energy eigenvalue of H_{λ_n} ;

$$H_{\lambda_n} | \Psi_n(\lambda_n) \rangle = E_n^{(0)}(\lambda_n) | \Psi_n(\lambda_n) \rangle \quad . \tag{4}$$

Now we compare the above result with the conventional approximation schemes. First of all, for $n = 0$, the first two terms become

$$\langle \Psi_0(\lambda_0) | H_{\lambda_0} + H' | \Psi_0(\lambda_0) \rangle = \langle \Psi_0(\lambda_0) | H | \Psi_0(\lambda_0) \rangle \quad , \tag{5}$$

which is just the conventional variational result of the ground state energy. The third term is the second order perturbation term which provides a systematic improvement over the simple variational ground state energy. We note that the perturbative correction term is negative for the ground state. Thus, it pushes down the variational values of the ground state energy for a better agreement with the true ground state energy. However, it should be noted that this correction might overcompensate the true ground state energy as observed in the anharmonic oscillator example in the next chapter. The approximate energy which combines the variational calculation and the second order perturbation correction no longer provides an upper bound to the exact ground state energy. The perturbation expansion of Eq.(3) is different from the conventional perturbation theory. The basis functions used in the perturbation are those obtained through a variational process and the eigenvalues are also optimized values.

Another important aspect of the present theory is that it can be readily applied in evaluating excited states unlike the conventional variational methods. In the usual variational calculation, for the calculation of an excited state energy, it is necessary to construct a trial wavefunction which is orthogonal to the ground state wavefunction, thus making the procedure rather cumbersome and difficult [4]. In the present formalism, it may appear that this requirement is automatically satisfied because $\Psi_n(\lambda_n)$ is the n th eigenfunction of H_λ , which is orthogonal to $\Psi_0(\lambda_n)$. However, this point requires a closer examination. Since λ_n is determined through minimization as given by Eq.(2), it is different for each n . For example, λ_0 should be used throughout in Eq.(3) for evaluation of the ground state energy, whereas λ_1 obtained from Eq.(2) should be used for evaluation of the first excited state. Therefore, the requirement of the orthogonality can be satisfied, but, in an approximate sense, because $\Psi_1(\lambda_1)$ is neither exactly orthogonal to the true ground-state wavefunction nor to $\Psi_0(\lambda_0)$. This point will be made more clear in the next chapters through examples.

III. ANHARMONIC OSCILLATOR

In this chapter, we apply the above formalism to the anharmonic oscillator problem which has a x^4 term. The Hamiltonian is given by

$$H = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2 + bx^4 \quad , \quad (6)$$

where b is positive. The conventional perturbative calculation is possible only when b is small [8]. In order to apply the present formalism to this problem, we should first find a suitable trial function and the corresponding parent Hamiltonian. A convenient choice is given by

$$\Psi_\Omega(\lambda) = \left(\frac{m\Omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\Omega}{2\hbar}x^2} \quad , \quad (7)$$

for the ground state trial wavefunction. Here Ω is a variational parameter. The corresponding parent Hamiltonian, which carries the above trial wavefunction as the exact ground state eigenfunction is given by

$$H_\Omega = \frac{p^2}{2m} + \frac{m\Omega^2}{2}x^2 \quad . \quad (8)$$

Using this parent Hamiltonian, we rewrite the original Hamiltonian,

$$\begin{aligned} H &= H_\Omega + H' \\ &= \frac{p^2}{2m} + \frac{m\Omega^2}{2}x^2 + \frac{m}{2}(\omega^2 - \Omega^2)x^2 + bx^4 \quad . \end{aligned} \quad (9)$$

We denote the n th eigenstate of H_Ω by $|n_\Omega\rangle$. Then the expectation value of $\langle n_\Omega|H|n_\Omega\rangle$ is given by

$$\begin{aligned} \langle n_\Omega| H |n_\Omega\rangle &= \langle n_\Omega|H_\Omega|n_\Omega\rangle + \langle n|H'|n\rangle \\ &= \langle n_\Omega|H_\Omega|n_\Omega\rangle - \frac{m(\Omega^2 - \omega^2)}{2}\langle n_\Omega|x^2|n_\Omega\rangle + b\langle n_\Omega|x^4|n_\Omega\rangle \\ &= \hbar\Omega\left(n + \frac{1}{2}\right) - \frac{\hbar(\Omega^2 - \omega^2)}{4\Omega}(2n + 1) + \frac{3b\hbar^2}{4m^2\Omega^2}(2n^2 + 2n + 1) \quad . \end{aligned} \quad (10)$$

Here, we used the standard quantum mechanical results [8];

$$\begin{aligned}\langle n_\Omega | x^2 | n_\Omega \rangle &= \frac{\hbar}{2m\Omega}(2n+1) , \\ \langle n_\Omega | x^4 | n_\Omega \rangle &= \left(\frac{\hbar}{2m\Omega}\right)^2(6n^2+6n+3) .\end{aligned}\quad (11)$$

By taking a variation on $\langle n_\Omega | H | n_\Omega \rangle$, we obtain a relation which determines Ω_n ,

$$\Omega_n^3 - \omega^2 \Omega_n - \frac{6b\hbar}{m^2} \frac{2n^2 + 2n + 1}{2n + 1} = 0 . \quad (12)$$

This equation is valid for any n . Now it is necessary to evaluate the third term of Eq.(3).

This second order calculation can also be carried out in a straightforward fashion [8] to yield

$$\begin{aligned}\sum_{k \neq n} \frac{|\langle k_\Omega | H' | n_\Omega \rangle|^2}{E_n^0(\Omega) - E_k^0(\Omega)} \\ = \frac{1}{4\hbar\Omega_n} \left(\frac{b\hbar^2}{4m^2\Omega_n^2}\right)^2 \frac{64n^5 + 160n^4 - 336n^3 - 664n^2 - 28n - 24}{(2n+1)^2} .\end{aligned}\quad (13)$$

Here, we used Eq.(12) to express $\Omega_n^2 - \omega_n^2$ in terms of Ω_n and b . Collecting terms, we obtain

$$\begin{aligned}E_n &= \frac{\hbar\Omega_n}{2}(2n+1) - \frac{3b\hbar^2}{4m^2\Omega_n^2}(2n^2+2n+1) \\ &+ \frac{1}{4\hbar\Omega_n} \left(\frac{b\hbar^2}{4m^2\Omega_n^2}\right)^2 \frac{64n^5 + 160n^4 - 336n^3 - 664n^2 - 28n - 24}{(2n+1)^2} .\end{aligned}\quad (14)$$

Now we can readily evaluate any energy eigenvalues of the anharmonic oscillator given by Eq.(6). First, we obtain Ω_n from Eq.(12) for a given n and substitute this value to Eq.(14).

In order to compare the present result with the conventional perturbation and the variational calculations, we carry out numerical calculations up to the second order using Eq.(14). For this purpose, we choose $\frac{m\omega^2}{2} = 0.5 \text{ eV \AA}^{-2}$ and carry out calculations for various values of b . The results for the ground state energy are shown in Table I. The exact ground state energy is obtained numerically using the Runge-Kutta-Fehlberg algorithm [9]. The result shows that the present method is clearly superior to the conventional perturbation theory and the variational calculation. First of all, the present method gives highly accurate values in the regime where the conventional perturbation theory is not applicable. This is because the perturbational basis has been renormalized through the variational process to yield a

better convergence. This renormalization effect can be also seen from the changing values of $\frac{1}{2}m\Omega^2$. For large b , $\frac{1}{2}m\Omega^2$ becomes much larger than $\frac{1}{2}m\omega^2$, thus making the perturbation Hamiltonian, $H' = -\frac{m(\Omega^2 - \omega^2)}{2}x^2 + bx^4$ correspondingly smaller. Now, in order to examine this behavior in detail, we show, in Table II, the results of the first and the second order calculations of the approximations for $b = 0.05eV\text{\AA}^{-4}$. First, we observe that in the ordinary perturbation theory, convergence is bad already. The first order result of the present approximation scheme is same to the variational calculation as shown in Eq.(3) and (5). We can see clearly that the renormalized perturbation calculation yields a good convergence.

We now extend the calculation to the first excited state energy. The results are shown in Table III. For $b = 0.05eV\text{\AA}^{-4}$, we obtain $E_1 = 5.092412eV$ which is 100.02% of the true value. Here, the variational parameter $\frac{1}{2}m\Omega_1^2$ is $0.990354eV\text{\AA}^{-2}$ and clearly different from $\frac{1}{2}m\Omega_0^2$. We note that the agreement for the first excited state is again excellent. As mentioned earlier, the value of the variational parameter, Ω , is different for each level.

IV. HELIUM ATOM

We now apply the present method to evaluate the energy eigenvalues of *He* atom. Evaluation of the ground state energy using both the standard perturbation method and the variational calculation are given in any standard quantum mechanical text books [1–4]. It is known that the standard perturbation calculation does not yield satisfactory result because of the large coulomb interaction between electrons. The variational approximation gives a better result, which will be utilized below.

The Hamiltonian for a *He* atom is given by

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} , \quad (15)$$

where Z is 2. In order to evaluate the energy eigenvalues variationally, we choose a parent Hamiltonian

$$H_{Z^*} = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Z^*e^2}{r_1} - \frac{Z^*e^2}{r_2} , \quad (16)$$

where Z^* is the variational parameter [1]. With this choice, the perturbation Hamiltonian H' is given by

$$H' = -\frac{(Z - Z^*)e^2}{r_1} - \frac{(Z - Z^*)e^2}{r_2} + \frac{e^2}{r_{12}} , \quad (17)$$

and $H = H_{Z^*} + H'$. The ground state eigenfunction for this parent Hamiltonian is given by

$$\Phi_0(Z^*) = \phi_{100}(Z^*, r_1)\phi_{100}(Z^*, r_2)\chi^- , \quad (18)$$

where $\chi^- = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)$. The expectation value of $\langle\Phi_0(Z^*)|H|\Phi_0(Z^*)\rangle$ is readily expressed as a function of Z^* [1],

$$\langle\Phi_0(Z^*)|H|\Phi_0(Z^*)\rangle = -\frac{1}{2}mc^2\alpha^2(4Z^*Z - 2Z^{*2} - \frac{5}{4}Z^*) . \quad (19)$$

The optimal value of Z^* is obtained by minimizing Eq.(19) and given by $Z^* = 1.6875$.

Substituting the above results to Eq.(3), we obtain

$$\begin{aligned} E_g = & -\frac{1}{2}mc^2\alpha^2(4Z^*Z - 2Z^{*2} - \frac{5}{4}Z^*) \\ & + \sum_k \frac{|\langle\Phi_k(Z^*)|H'|\Phi_0(Z^*)\rangle|^2}{E_g^0(Z^*) - E_k^0(Z^*)} \\ & + \dots \end{aligned} \quad (20)$$

The first term gives the usual variational result, $E_g = -5.6953ryd$ for the ground state energy which is 98.077% of the experimental value of -5.8070 [1]. In calculating the second order contribution, we only have to consider excited state wavefunctions which have antisymmetric spin parts, since $\Phi_0(Z^*)$ is antisymmetric in spins. The general form of the wavefunction with antisymmetric spin parts is given by

$$\Phi_{n'l'm'}^{nlm}(r_1, r_2) = A[\phi_{nlm}(r_1)\phi_{n'l'm'}(r_2) + \phi_{n'l'm'}(r_1)\phi_{nlm}(r_2)]\chi^- , \quad (21)$$

where $A = \frac{1}{\sqrt{2}}$ if $nlm \neq n'l'm'$ and $\frac{1}{2}$ if $nlm = n'l'm'$. For calculation of the second order term, we divide the perturbation Hamiltonian, H' , into two parts

$$H'_1 = -\frac{(Z - Z^*)e^2}{r_1} - \frac{(Z - Z^*)e^2}{r_2} ,$$

and

$$H'_2 = \frac{e^2}{r_{12}} . \quad (22)$$

The H'_1 contribution does not have any angular dependence. Therefore, it can be straightforwardly calculated to yield

$$\begin{aligned} \langle \Phi_{n'l'm'}^{nlm} | H'_1 | \Phi_{100}^{100} \rangle \\ = -2A(Z - Z^*)e^2\delta_{lm,00}\delta_{l'm',00}(X_n\delta_{n',1} + X_{n'}\delta_{n,1}) , \end{aligned} \quad (23)$$

where

$$X_n = \int dr r^2 R_{n0}(r) \frac{1}{r} R_{10}(r) .$$

The H'_2 contribution can be calculated by expanding $\frac{1}{|r_1 - r_2|}$ in terms of spherical harmonics [3]. A lengthy but straightforward calculation yields the result

$$\langle \Phi_{n'l'm'}^{nlm} | H'_2 | \Phi_{100}^{100} \rangle = \frac{2Ae^2(-1)^m}{2l+1} \delta_{l,l'} \delta_{m,-m'} Y_{nn'l} , \quad (24)$$

where

$$Y_{nn'l} = \int dr dr_2 r_1^2 r_2^2 R_{nl}(r_1) R_{n'l}(r_2) \frac{r_{\leq}^l}{r_{>}^{l+1}} R_{10}(r_1) R_{10}(r_2) . \quad (25)$$

Collecting the above results, we obtain an expression for the ground state energy,

$$\begin{aligned} E_g = & -\frac{1}{2}mc^2\alpha^2(4Z^*Z - 2Z^{*2} - \frac{5}{4}Z^*) \\ & + \sum_{n,n',l,m} \frac{|\langle \Phi_{n'l-m}^{nlm} | H' | \Phi_{100}^{100} \rangle|^2}{-\frac{1}{2}mc^2(Z^*\alpha)^2[2 - \frac{1}{n^2} - \frac{1}{n'^2}]} , \end{aligned} \quad (26)$$

where

$$\begin{aligned} |\langle \Phi_{n'l-m}^{nlm} | H' | \Phi_{100}^{100} \rangle|^2 \\ = | -2A(Z - Z^*)e^2\delta_{lm,00}(X_n\delta_{n',1} + X_{n'}\delta_{n,1}) \\ + \frac{2Ae^2(-1)^m}{2l+1} \delta_{lm,l'-m'} Y_{nn'l} |^2 . \end{aligned} \quad (27)$$

Here, we assume $n' \geq n$, $0 \leq l \leq n - 1$, and $0 \leq m \leq l$. Also $n' = n = 1$ should not be included in the second order correction. The above expression is numerically evaluated upto $n' = 7$. The second order correction gives $-0.0249ryd$, and, thus, makes the total ground state energy $-5.7202ryd$, which is 98.505% of the experimental value of -5.8070 . Comparing to the original variational calculation value of -5.6953 , we observe that a systematic improvement has been achieved, although the agreement is not as good as the case of anharmonic oscillator. We believe that this rather slow convergence may originate from the fact that we used the same Z^* for both electrons. It is known that if one electron draws closer to the nucleus at some instant, it tends to push the other farther out, thus making the screened charges different for the two electrons [1]. Also using the same Z^* for excited states may introduce additional errors. However, either introducing an additional variational parameter or calculating Z^* for each excited level would make the present scheme too complicated to be useful. We just note that for the first excited state of symmetric spin state, Z^* is given by 1.8497 which is quite different from that of the ground state. The first excited state energy obtained variationally without the second order correction is given $-4.2765 ryd$ comparing to the experimental value of $-4.3504 ryd$. Because of computational complexity, we have not carried out the full second order calculation. However, partial calculations with some selected terms also show the same trends as in the case of the ground state.

V. CONCLUSIONS

We have presented an approximation scheme which combines the perturbation theory with the variational calculation in quantum mechanics. It is shown that this scheme provides a very good convergence beyond the first variational calculation even when the perturbing potential is large. Also it can be readily used to estimate excited states. Therefore, this method overcomes the shortcomings of the perturbation theory and the variational calculation and combines the advantages, when applicable. Here, it should be noted that the present method is applicable only when a parent Hamiltonian can be found, thus limiting

its usefulness. However, it is known that for a quite large number of problems, potentials can be expanded into simple harmonic potential plus higher order terms. In such category of problems, the present method is expected to be efficient.

Another merit of the present method which, we believe, may be more important is the pedagogical value of the combined approximation scheme. The theory shows to the students the limits of both approximations and demonstrates a way to overcome those, although in a limited class of problems. Also, this method provides an easy example of renormalized perturbation theory which are often used in many body and field theories [10].

ACKNOWLEDGMENTS

This work has been partially supported by the Korean Ministry of Education (BSRI-97-2425), the Korea Science and Engineering Foundation through Project No. 95-0701-04-01-3 and also through the SRC program of SNU-CTP, and Yonsei University Research Fund.

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TABLES

TABLE I. Comparison of the ground state energies(in eV) obtained using different approximation schemes.The values in the parentheses are the ratios to the exact values. The values of $\frac{1}{2}m\Omega_0^2$ are also shown as references.

$b(\text{eV}\text{\AA}^{-4})$	0.01	0.05	0.25
Perturbation Theory	1.4318427 (99.935%)	1.5279252 (95.962%)	does not converge.
Variational Calculation	1.4333279 (100.038%)	1.5968858 (100.293%)	2.0664772 (100.929%)
Present Method	1.4327276 (99.997%)	1.5912088 (99.937%)	2.0412648 (99.679%)
Exact Energy Value	1.4327725	1.5922195	2.0474629
$\frac{1}{2}m\Omega_0^2(\text{eV}\text{\AA}^{-2})$	0.5770839	0.8227827	1.6423320

TABLE II. Detailed comparison of the ground state energy values (in eV) obtained by different methods for $b=0.05 \text{ eV}\text{\AA}^{-4}$.

Method of Approximation	First order calculation	Second order calculation
Perturbation	1.6659633 (104.632%)	1.5279252 (95.962%)
Variational Calculation	1.5968858 (100.293%)	—
Present Method	1.5968858 (100.293%)	1.5912088 (99.937%)

TABLE III. Comparison of the first excited state energies (in eV) for $b=0.05\text{eV}\text{\AA}^{-4}$. The values in the parentheses are ratios to the exact value. The value of $\frac{1}{2}m\Omega_1^2$ is shown together as a reference.

Perturbation	4.484801(88.09%)
Variational Calculation	5.106102(100.29%)
Present Method	5.092412(100.02%)
Exact Value	5.091282
$\frac{1}{2}m\Omega_1^2(eV\text{\AA}^{-2})$	0.990354